Solubility in CO₂ and carbonation studies of epoxidized fatty acid diesters: towards novel precursors for polyurethane synthesis[†]

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Novel linear polyurethanes were synthesized by bulk polyaddition of diamines with two vegetable-based biscarbonates produced from oleic acid methyl ester. Internal carbonated fatty acid diester (ICFAD) and terminal carbonated fatty acid diester (TCFAD) were obtained by the reaction of their epoxide precursors with CO₂. Terminal epoxy fatty acid diester (TEFAD) was found to be more soluble and more reactive in CO₂ than internal epoxy fatty acid diester (IEFAD). Polyurethanes obtained by polyaddition of TCFAD and ICFAD with diamines exhibit molecular weights up to 13 500 g mol⁻¹ and glass transitions around -15 °C. Amide linkages were not observed when secondary diamine was used as the comonomer.

Introduction

With an annual world production of about 10 wt%, polyurethanes (PUs) represent an important class of polymer materials, widely used in many fields either as cross-linked materials or as thermoplastics (TPU). The latter can be obtained as highly resilient flexible foams, durable elastomeric materials, high performance adhesives and sealants, medical devices, etc.¹ Most PUs are generally obtained from the tin-catalyzed polyaddition reaction between synthetic polyols and polyisocyanates. Due to the uncertain cost of petroleum in the near future as well as the need to develop sustainable chemical routes, the use of renewable resources such as vegetable oils and fats for the synthesis of polymers is currently expanding.²⁻⁵ Many types of vegetable oil such as naturally hydroxylated ricinoleic oil and also rapeseed oil, tung oil, linseed oil, canola oil, sunflower oil and soybean oil have already been reported as sources of polyols for PU synthesis. These vegetable-based polyols have been found to be good substitutes to synthetic ones, giving rise to PUs with versatile and competitive thermo-mechanical properties.

The chemical modification of unsaturated vegetable oils (triglycerides) to synthesize polyols is described in the literature. Hydroxylation⁶⁻⁹ or hydroformylation^{10,11} of the double bonds, ozonolysis¹² and transesterification^{13,14} are the main reactions studied. Despite the interest in developing new vegetable-based polyols, the use of toxic polyisocyanates, manufactured from

phosgene, remains an important issue to overcome. Therefore, the development of alternative methods for the preparation of PUs which avoid the use of phosgene is of high interest. Recently, Narine and co-workers investigated the production of a new linear saturated terminal diisocyanate synthesized from oleic acid.¹⁵ Cramail and co-workers have also recently reported the synthesis of polyurethanes from oleic and ricinoleic acids using an AB-type self-condensation polymerization route from α -hydroxyl, ω -acyl-azido precursors.¹⁶ Another non-isocyanate route to PUs involves the reaction of polyamines with polycarbonates, the latter being obtained by the reaction of polyapoxides with CO₂, leading to non-isocyanate polyurethanes (NIPUs).¹⁷⁻²⁰ An important benefit of this chemical pathway is to substitute phosgene by CO₂, an abundant, renewable and environmentally friendly chemical.

Epoxidized vegetable oils (triglycerides) are good raw materials for carbonation. Wilkes *et al.* converted epoxidized soybean oil (ESBO) into carbonated soybean oil (CSBO) in 70 h at atmospheric pressure and 110 °C, in the presence of tetrabutylammonium bromide (TBABr) as the catalyst.²¹ The authors also investigated the synthesis of NIPU networks by reacting CSBO with different diamines. The yield and kinetics of carbonation was later improved by Doll *et al.* thanks to the use of supercritical carbon dioxide, scCO₂.^{22,23} Rokicki and coworkers also used CSBO to modify a bisphenol-A based epoxy resin.²⁴ The effect of CSBO content on the curing behaviors and the thermal and mechanical interfacial properties of the epoxy resin/CSBO composition was analyzed.

Literature data mainly relates to PU synthesis from carbonated triglycerides. The high functionality and the varied molecular structures of these carbonated triglycerides give rise to rather ill-defined cross-linked PU materials. All these considerations prompted us to investigate the use of well-defined bis-carbonated vegetable-based precursors, for the synthesis of linear polyurethanes (TPUs). To that purpose, we have designed two new epoxidized fatty acid diesters (EFADs) (see Scheme 1), terminal and internal epoxidized fatty acid diesters (TEFAD and IEFAD), respectively.

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Scheme 1 Reaction scheme of IEFAD and TEFAD synthesis.

In the first part of this study, we investigate (through *in situ* FTIR monitoring) the mutual miscibility of CO₂ and the two EFADs as well as the optimal conditions for the carbonation reaction in the presence of TBABr as the catalyst, with respect to temperature and CO₂ pressure. It is worth noting that thermodynamic models and interaction parameter values of different vegetable oils in supercritical carbon dioxide have already been reported²⁵⁻³¹ but, to our knowledge, never for epoxidized oils. In the second part of the study, the synthesis of polyurethanes from the so-formed carbonated fatty acid diesters (CFAD) and two diamines (ethylenediamine and isophorone diamine) is discussed. *In situ* ATR-FTIR spectroscopy was found to be a useful technique to follow the formation of polyurethanes as a function of temperature and the nature of the diamines.

Experimental section

Materials

IEFAD and TEFAD precursors have been synthesized from oleic fatty acid methyl ester from sunflower oil (Scheme 1).³² The purity of each EFAD, determined by ¹H NMR was close to 95%. Tetrabutylammonium bromide (TBABr), ethylenediamine (EDA) and isophorone diamine (IPDA) were purchased from Sigma Aldrich and used as received. Carbon dioxide N45 (purity 99,95%) was supplied by Air Liquide.

Analysis

The IR measurements were performed on a Thermo-Optek interferometer (type 6700) equipped with a globar source, a Ge/KBr beam splitter and a DTGS detector. Single beam spectra recorded in the spectral range 400–7500 cm⁻¹ with a 2 cm⁻¹ resolution were obtained by Fourier transformation of 50 accumulated interferograms. The *in situ* phase behavior investigations were performed using a home-made stainless

steel cell equipped with four cylindrical sapphire windows, two windows for the infrared absorption measurements with a path length of 7.2 mm and two sapphire windows for direct observation of the solution.³³ Using such windows, one can access the wavenumber range from 2500 to 7500 cm⁻¹. For the kinetic study of the carbonation reaction, we have used germanium windows with a path length of 100 µm instead of sapphire ones in order to measure the infrared spectra in the wavenumber range extending from 700 to 5000 cm⁻¹. The windows were positioned on the flat surface of the plug. A 100 µm Kapton[®] foil placed between the window and the plug compensated for any imperfections between the two surfaces. Flat Teflon[®] seals insured a seal between the plug and the cell body. Heating was achieved by using four cartridge heaters distributed throughout the body of the cell in which two thermocouples were placed. The first one located close to one cartridge is used for the temperature regulation and the second was kept close to the sample area in order to measure the temperature of the sample with an accuracy of about $\Delta T \sim$ ± 0.5 °C. The cell was connected *via* a stainless steel capillary to a hydraulic pressurizing system which allows the pressure to be raised up to 50 MPa with an absolute uncertainty of ±0.1 MPa and a relative error of $\pm 0.3\%$.

The kinetics of polyurethane synthesis from the polyaddition of carbonated fatty acid diesters (CFADs) with the two diamines (EDA and IPDA) were carried out by means of *in situ* ATR-FTIR spectroscopy by using a ThermoOptek 6700 spectrometer and a heatable Golden Gate diamond ATR accessory (Specac). The CFAD was mixed with the diamine, and a small droplet of the mixture was deposited 5 minutes later on the ATR crystal, which was preheated to the appropriate temperature. Infrared spectra with a spectral resolution of 4 cm⁻¹ were taken every 10 min over a period of 24 h.

Size exclusion chromatography (SEC) analyses were performed on polyurethane samples before precipitation, at room temperature, in THF with a setup consisting of a WATERS 880-PU pump and a series of three microstyragel columns with pore sizes of 103, 105 and 106 Å. The eluate of the filtered samples was monitored using simultaneous UV and refractive index detections. The elution times were converted to molecular weight using a calibration curve based on low dispersity (M_w/M_n) polystyrene (PS) standards. The differential scanning calorimetry (DSC) thermograms were measured using a DSC Q100 apparatus from TA instruments. Polymer samples were first heated from -100 to 200 °C and the glass transition temperatures were determined after the second heating run. All runs were performed at a heating rate of 10 °C min⁻¹.

Experimental procedure

In order to determine the EFAD concentration in the CO₂rich phase, the lower part of the cell was first partially filled with EFAD in order to get its level well below the incoming infrared beam (see Fig. 1a). For the determination of the EFAD and CO₂ concentration in the oil-rich phase as a function of temperature and CO₂ pressure, the cell was filled to a level above the incoming beam (see Fig. 1b). In each case, the cell was then heated up to the required temperature. The spectra were recorded for the raw EFAD, then CO₂ was added up to the



Fig. 1 Schematic drawing of the *in situ* experiment using a transmission optical cell to study a) the concentration of EFAD in CO_2 phase and b) the CO_2 sorption and EFAD swelling.

highest desired pressure. The system was kept under isobaric and isothermal conditions for about 15 min in order to ensure that the equilibrium was achieved. The stabilization of the operating conditions was controlled by recording consecutive spectra. The mixture was constantly homogenized during the experiment using a magnetically driven stirrer positioned at the bottom of the cell.

For the kinetic study, the experimental procedure was almost the same except that the catalyst (TBABr, 3 wt%) was first dissolved in the EFAD-rich phase and the *in situ* FTIR monitoring was started immediately after the injection of CO_2 at the selected pressure and temperature. One infrared spectrum was recorded every 10 min.

Results and discussion

Phase behaviour of the EFAD-CO₂ system

Infrared absorption spectra. The infrared spectra of both EFADs (IEFAD and TEFAD) and the CO₂-rich phases of the EFAD/CO₂ mixtures were recorded for a range of pressures up to 20 MPa at temperatures from 25 to 120 °C. Fig. 2 illustrates (for the case of IEFAD) the spectral changes in the CO₂-rich phase that occur with an increase of CO₂ pressure. A number of significant peaks associated with combination bands of CO₂ and fundamental stretching modes of EFAD can be observed. The intensities of these peaks increase with CO₂ pressure indicating an increase of the CO₂ density and the EFAD solubility in the CO₂-rich phase. The peak centered at 2860 cm⁻¹, associated with the CH stretching vibrations of EFAD, can be used to determine the solubility of EFAD in CO₂. In the same manner, Fig. 3 illustrates the spectral changes of the IEFAD-rich phase in the



Fig. 2 IR spectra of IEFAD in the CO_2 -rich phase at 5 MPa (black), 15 MPa (red) and 20 MPa (blue), at 70 °C.



Fig. 3 IR spectra of IEFAD in the oil-rich phase at 7.5 MPa (black), 15 MPa (red) and 20 MPa (blue), at 70 $^{\circ}$ C.

wavenumber range 4600–6000 cm^{-1} that occur with an increase of CO₂ pressure.

A number of significant peaks associated to the combination or overtones of EFAD can be observed in the spectral range $5200-6000 \text{ cm}^{-1}$. Increasing the CO₂ pressure leads to a decrease in the intensities of the EFAD bands (for example at 5690 and 5800 cm^{-1}), whereas the intensity of the CO₂ peaks, characteristic of CO₂ sorbed into EFAD (for example at 4950 cm⁻¹), increases.

As the more intense peak observed in Fig. 3 centred at 5800 cm^{-1} is sometimes saturated in our experimental conditions, the peak centred at 5690 cm^{-1} was used to determine the concentration of the EFAD subjected to scCO₂.

Concerning CO₂, one can detect three peaks at 4800, 4950 and 5100 cm⁻¹ which are assigned to the combination modes $4v_2+v_3$, $v_1+2v_2+v_3$, and $2v_1+v_3$ of the CO₂ molecule respectively.³⁴ Due to the weak intensity of the peaks at 4800 and 5100 cm⁻¹, the band at 4950 cm⁻¹ was used to estimate the variation of the CO₂ concentration incorporated into the EFAD-rich phase as a function of the CO₂ pressure.

Data processing for the determination of the mutual solubility of EFAD and CO₂. In order to determine the concentration of EFAD in the CO₂-rich phase, the peak centered at 2860 cm⁻¹ associated with CH stretching vibrations of EFAD was selected. The peak height of these characteristic infrared bands allows us to determine the concentration of the solute according to the Beer–Lambert law, $A = \varepsilon$. *l. c* where A is the sample absorbance; ε the molar extinction coefficient (L mol⁻¹ cm⁻¹); l, the optical path length (cm) and c the sample concentration (mol L^{-1}). In this study, the peak height was used instead of integrated area because of the superposition of another CH band in the same spectral region, which could lead to a poor quality determination of the component area. Also, the baseline correction may produce larger errors when the integrated area method is used. In order to determine the concentration of EFAD from the peak intensity, we have first determined the molar extinction coefficient for the relevant band (see Table 1) by recording the infrared spectra of EFAD solutions in CCl₄ with known concentrations. The use of an apolar solvent such as CCl₄ is not expected to have a significant influence on the molar extinction coefficient.

Group frequency	IEFAD				TEFAD				CO ₂
	$v_{\rm c} =_{\rm o}$	$v_{ m C-H}$	$v_{\rm C-H}$ + $\delta_{\rm C-H}$	$2v_{\text{C-H}}$	$v_{c}=_{o}$	$ u_{ m C-H}$	$v_{\text{C-H}} + \delta_{\text{C-H}}$	$2v_{\text{C-H}}$	$\overline{v_{1+} 2v_{2+} v_3}$
Wave number/cm ⁻¹ ε (<i>L</i> mol ⁻¹ . cm ⁻¹)	1736 1069	2857 821	4263 4.73	5690 2.60	1736 1127	2863 829	4263 7.42	5711 1.51	4960 0.21

Table 1 Molar extinction coefficient of IEFAD, TEFAD and CO₂ for different absorption bands

In order to estimate the EFAD concentration in the EFADrich phase swelled with CO_2 , the same procedure as described above was followed. In this case, the peak height of the band centred at 5700 cm⁻¹ which is associated to an overtone of the CH vibrations of EFAD was considered. The molar extinction coefficient for this band (reported in Table 1) was determined from the spectrum measured under ambient conditions for pure EFAD for which the density (or concentration) was known.

Finally, the concentration of CO₂ (C_{CO2}) incorporated into the EFAD phase was calculated using the peak height of the $v_1+2v_2+v_3$ band of CO₂ centred at 4950 cm⁻¹.

The molar absorption coefficient displayed in Table 1 was estimated by measuring the infrared spectra of supercritical CO_2 for a range of temperatures and pressures, and the corresponding densities (or concentrations) were available from the literature.³⁵ It was assumed that the molar absorption coefficient of this peak was the same when CO_2 swells the EFAD molecule.

Solubility of epoxy fatty acid diester (EFAD) in CO₂. Fig. 4 displays the concentration of TEFAD and IEFAD in the CO₂-rich phase as a function of pressure at different temperatures. Whatever the temperature, the solubility of both EFADs is negligible at pressures below 10 MPa and then increases strongly above this threshold. This effect is particularly clear at low temperature. Although the concentration values are quite low, the EFADs studied have a significant solubility in supercritical CO₂. For a given pressure, a temperature increase causes a decrease in solubility of both EFADs. For a given (P, T) couple, the solubility of TEFAD in the CO₂-rich phase is higher than that of IEFAD.



Fig. 4 Concentration of TEFAD and IEFAD in the CO_2 -phase as a function of the pressure, at different temperatures (70 °C and 80 °C for IEFAD). Insert: concentration of TEFAD in the CO_2 -phase as a function of the pressure and temperature.

In order to discriminate the temperature and pressure effects, the concentration of TEFAD and IEFAD as a function of

the density has been studied for different temperatures (Fig. 5). Whatever the temperature, the higher the CO_2 density, the higher the solubility of both EFADs. For a given density, the temperature effect seems to be almost negligible. Therefore, it appears that the driving force that affects the solubility of such EFAD molecules in CO_2 is the density of the supercritical medium. In order to examine this point, we have compared on Fig. 6 the solubility of TEFAD and IEFAD with that of a glyceride series.



Fig. 5 Concentration of TEFAD and IEFAD in the CO_2 -phase as a function of the CO_2 density.



Fig. 6 Ln[EFAD] as a function of the density of CO₂ at 50 °C. Comparison with literature data $(T = 50 \text{ °C})^{36}$.

This series is composed of oleic acid, monolein (ester of glycerol with one C18:1 chain), diolein (ester of glycerol with two C18:1 chains) and triolein (triglyceride with three C18:1 chains). The latter data was reported in the literature as a function of the density of supercritical CO₂ at T = 50 °C.³⁶ Concerning the glyceride series, the difference in polarity and molecular weight of the tested molecules was shown to affect the vapor pressures

and thus the solubility in CO_2 . Monoglyceride is logically more soluble in CO_2 than diglyceride and triglyceride because of its lower carbon number. The solubilities of TEFAD and IEFAD were found to be in-between oleic acid and monoglyceride. The lower molecular weight of TEFAD (468 g mol⁻¹) versus that of IEFAD (664 g mol⁻¹) explains its higher solubility in CO_2 . Due to its lower molecular weight (282 g mol⁻¹), oleic acid is the most volatile and thus the most soluble in CO_2 of the entire series. The lower solubility of monoglyceride (355 g mol⁻¹) compared to oleic acid is also explained by its higher polarity due to the presence of the two hydroxyl groups. Despite its lower molecular weight, its solubility is close to that of TEFAD and IEFAD.

Swelling of epoxy fatty acid diester by CO₂. The swelling of TEFAD and IEFAD in the EFAD-rich phase as a function of CO₂ pressure at T = 50 °C and 80 °C for IEFAD and at T = 50 °C to 120 °C for TEFAD is reported in Fig. 7. The swelling S is the ratio of the initial concentration (C₀) versus the concentration (C) at a given CO₂ pressure: [$S = (C_0/C) -$ 1]. The highest swelling is obtained for TEFAD in comparison to IEFAD. The swelling of both EFADs increases significantly with pressure up to a value of about 60% reached for a pressure of 20 MPa at 50 °C. For a given pressure, an increase of the temperature yields a decrease of the EFAD swelling. This data clearly shows that CO₂ is able to penetrate into the epoxidised oils (EFADs), resulting in a swelling of the EFAD phase which is significantly higher than that usually measured for polymers³⁷ but lower than that reported for common solvents.³⁸



Fig. 7 Swelling of TEFAD and IEFAD as a function of the CO₂ pressure at different temperatures.

Kinetic study of epoxy fatty acid diester carbonation reaction

The kinetics of the carbonation reaction (Scheme 2) was studied by varying the pressure of CO_2 (from 5 MPa up to 18.5 MPa) and the temperature (from 60 °C up to 140 °C). Fig. 8 and Fig. 9 illustrate the spectral changes of EFAD in the wavenumber range 600–4500 cm⁻¹ that occur with the carbonation of epoxy groups. One can detect the formation of two bands corresponding to carbonate groups, one at 1803 cm⁻¹ and one at 772 cm⁻¹. Another significant peak at 826 cm⁻¹ is associated to the disappearance of the epoxy groups. The reaction progress was monitored by the height of the carbonate band at 772 cm⁻¹ and the epoxy band at 826 cm⁻¹ (the peak at 1803 cm⁻¹ becomes saturated after a



Scheme 2 Reaction scheme of IEFAD and TEFAD carbonation.



Wave number (cm⁻¹)

Fig. 8 In situ IR monitoring of the carbonation reaction of IEFAD into ICFAD at 80 °C and 10 MPa.



Fig. 9 IR spectra of *in situ* carbonation monitoring of IEFAD at 80 $^{\circ}$ C and 10 MPa. The spectrum of the IEFAD precursor (black) and the spectrum recorded after 25 min reaction time (red). Insert: changes in the peak height of the carbonate band (772 cm⁻¹) and epoxy band (826 cm⁻¹) at different reaction times.

few minutes into the reaction). In order to determine the EFAD conversion into the carbonated fatty acid diester (CFAD), the height of the peak at 772 cm⁻¹ was converted into a percentage.

Influence of the temperature. First, the pressure was fixed at 10 MPa to study the influence of the temperature on the

kinetics of carbonation. All the runs were stopped after 100 min into the reaction by depressurizing the cell. Fig. 10 (blue tags) displays the conversion of EFAD into CFAD—based on the intensity of the growing carbonate band at 772 cm⁻¹—for both TEFAD and IEFAD at different temperatures ranging from 60 °C to 140 °C. As expected, the temperature has a dramatic effect on the reaction kinetics for both EFADs. Fig. 10 clearly shows the faster kinetics of TEFAD conversion with respect to IEFAD, a phenomenon explained by the higher reactivity of the terminal epoxide groups compared to internal ones. As an example, after 100 min, 92% of the TEFAD is converted at 100 °C in comparison to 45% for IEFAD. As a conclusion, a temperature increase of up to 140 °C is required to get complete conversion with IEFAD, compared to 120 °C in the case of TEFAD.



Fig. 10 Percentage of carbonation of TEFAD and IEFAD respectively as a function of the pressure at 120 $^{\circ}$ C (in red) and as a function of the temperature at 10 MPa (in blue), after 100 min into the reaction.

Influence of the pressure. Second, the temperature was fixed at 120 °C and the carbonation was performed at pressures ranging from 5 MPa to 18.5 MPa. The conversion of IEFAD into ICFAD is strongly affected by the CO_2 pressure (see Fig. 10, red tags). The conversion is maximal at 10 MPa (90%) and above this optimal value, increasing the pressure does not favor the conversion of epoxide groups into carbonate groups.

In the case of TEFAD, the conversion of epoxy groups into carbonate ones is almost unaffected by the CO_2 pressure at this temperature and varies between 94% and 100%. As already discussed, this is explained by the higher reactivity of the epoxy groups in terminal positions. Whatever the conditions (*P*, *T*, 100 min), the conversion of TEFAD into TCFAD is always higher than that of IEFAD into ICFAD.

Synthesis of polyurethanes from CFAD and diamines

Kinetics of CFAD polymerization. ICFAD and TCFAD were both polymerized in bulk with ethylenediamine (EDA) and

isophoronediamine (IPDA) (stoichiometric ratio, [carbonate] = $[NH_2]$), at different temperatures, in the absence of catalyst (Scheme 3). As it is illustrated in Fig. 11 for the case of ICFAD and IPDA as monomers, the polyadditions were monitored by *in situ* ATR-FTIR spectroscopy, using the disappearance of the carbonate bands at 1803 and 772 cm⁻¹ and the appearance of new bands at 3330, 1714 and 1530 cm⁻¹, assigned to the hydroxyl group, carbonyl group and N–H deformation of the urethane function, respectively.



Scheme 3 Polyurethane synthesis by polyaddition between CFAD and diamines.



Fig. 11 In situ ATR-IR monitoring of the polyaddition at 70 °C between ICFAD and IPDA as a function of time.

Fig. 12 represents the decrease of the carbonate band absorbance at 1803 cm⁻¹ as a function of time, at 70 °C and 110 °C in the case of CFAD/IPDA and CFAD/EDA polyadditions. As expected, an increase of the temperature eases the conversion of the carbonate groups into urethane functions. Fig. 12 also highlights the higher reactivity of TCFAD in comparison to ICFAD proving that terminal carbonate groups are much more reactive than internal ones. In the case of the ICFAD/IPDA system, the conversion is complete after 12 h at 110 °C in comparison to 9 h with TCFAD/IPDA. One can also notice that the rate of carbonate conversion is much more sensitive to the temperature increase in the case of ICFAD polymerizations. Finally, when EDA was used as comonomer, the conversion of the carbonate function did not reach completion (pink curve),



Fig. 12 Kinetics of CFAD/IPDA and CFAD/EDA polyadditions as a function of time at 70 °C and 110 °C determined by the decrease of the carbonate band at 1803 cm⁻¹.

and this behavior is explained by the occurrence of side reactions (see next section).

Influence of the diamine structure. In recent work dealing with PU synthesis through a carbonate route, Petrovic and coworkers reported the occurrence of a side reaction between the diamines used (EDA and butylenediamine (BDA)) with the ester function of the vegetable oil, resulting in the formation of amide groups and thus affecting the final polymer structure.³⁹ This reaction was favoured by increasing the temperature of polymerization (from 70 °C to 100 °C). In this work, the formation of amide functions was found to be affected by the type of diamine used. Indeed, while no amide groups were detected in the case of IPDA, in contrast, one could observe that some of the ester groups were converted into amide functions when EDA was used as the comonomer. The formation of these amide groups was revealed by IR spectroscopy with the appearance of a specific band at 1655 cm⁻¹ as indicated in Fig. 13.

The ¹H NMR spectrum of ICFAD together with that of the PU obtained from reaction between ICFAD and EDA are represented in Fig. 14. New peaks at 3.6 and 4.6 ppm reveal the formation of the urethane linkage (e) and hydroxyl group (f). Nevertheless, signals at 4.2 and 4.5 ppm corresponding to the protons **a** of the carbonate group have not completely disappeared at the end of the reaction, which confirms the presence of residual carbonate groups. The presence of amide groups is characterised by the appearance of peaks at 2.1 ppm, related to protons **g**. Integration of these peaks reveals that 22% of amide groups are formed. In conclusion, IPDA appeared to be advantageously selective for carbonate *versus* ester groups, avoiding the formation of amide linkages. Such a side reaction is favored when using more reactive primary amines, such as EDA, in agreement with literature data.

PU average molecular weights. The so-formed PUs were found to be soluble in THF enabling the determination of their average molecular weights in this solvent, against a polystyrene calibration. The data are collected in Table 2. For a given couple of monomers, raising the temperature from 70 °C to 110 °C leads to an increase in polyurethane average molecular weight. In agreement with the higher reactivity of TCFAD



Fig. 13 ATR-IR spectra of ICFAD (blue), polyurethane formed by reaction of ICFAD with IPDA at 70 $^{\circ}$ C (red) and polyurethane formed by reaction of ICFAD with EDA at 70 $^{\circ}$ C (black).



Fig. 14 ¹H NMR spectra of ICFAD and of PU obtained after reaction between ICFAD and EDA at 70 °C.

in comparison to ICFAD, the highest PU molecular weights were obtained with the TCFAD/IPDA monomer couple at 110 °C ($M_w = 13500$ g mol⁻¹). The dispersity M_w/M_n of the polyurethane samples remain narrow, below 1.5, that can be probably explained by incomplete conversion. It is worth noting

Monomers $T/^{\circ}C$	Total conv."	$M_{ m w}/{ m g}$ mol ⁻¹ ^b	$M_{ m w}/M_{ m n}$	% Amide ^c	$T_{\rm g}/^{\circ}{ m C}^{d}$
ICFAD/EDA 70	3 h	4 300	1.1	22	-25
ICFAD/IPDA 70	20 h	9 1 0 0	1.3		-21
ICFAD/IPDA 110	12 h	11700	1.4		-19
TCFAD/IPDA 70	12 h	10700	1.4		-16
TCFAD/IPDA 110	9 h	13 500	1.5		-13

^{*a*} At complete disappearance of the carbonate band at 772 cm⁻¹, except for poly(ICFAD/EDA) because of residual carbonate groups. ^{*b*} SEC, solvent THF, PS calibration. ^{*c*} Determined by ¹H NMR (integration of peaks at 2.1 ppm). ^{*a*} DSC, temperature ramp from -100 °C to 200 °C, at 10 °C min⁻¹.

that PUs obtained from polyadditions of ICFAD with EDA exhibit much lower molecular weights, explained by a loss of amine functions through the formation of amide linkages. Fig. 15 shows the SEC traces of polyurethanes obtained from TCFAD and IPDA (poly[TCFAD-IPDA]) and from ICFAD and IPDA (poly[ICFAD-IPDA]), both at 110 °C. It also reveals the absence of residual monomer in the PU samples.



Fig. 15 SEC traces of TCFAD (red), ICFAD (black), PU obtained by polyaddition of ICFAD with IPDA at 110 °C (green) and PU obtained by polyaddition of TCFAD with IPDA at 110 °C (blue). Solvent: THF; PS calibration.

Thermo-mechanical analysis of PU samples. The linear PUs were analyzed by differential scanning calorimetry (DSC). All samples exhibit one glass transition temperature, T_g , ranging from -25 °C to -13 °C. PUs obtained from ICFAD exhibit a T_g that is systematically lower than that of PUs from TCFAD, a phenomenon explained by the slightly lower molecular weight of these PUs but also by the presence of pendant chains (C_8H_{17}) which can act as plasticisers.

As expected, the T_g of all these linear PUs are lower than those of cross-linked soy-based PUs obtained from carbonated triglycerides and EDA, that display a T_g around 20 °C.³⁹

Conclusions

In this study, novel linear polyurethanes were synthesized by bulk polyaddition of diamines with vegetable-based biscarbonates, namely ICFAD and TCFAD, produced from oleic acid methyl ester. ICFAD and TCFAD were obtained by the reaction of their epoxide precursors (IEFAD and TEFAD) with CO₂. The phase behavior of the EFAD/CO₂ mixtures was first studied with respect to temperature (70–110 °C) and pressure (5–20 MPa). TEFAD was found to be more soluble than IEFAD in the CO_2 -rich phase, certainly because of its lower molecular weight and greater volatility. The concentration of CO_2 was also slightly higher in the TEFAD-rich phase than in the IEFAD-rich one. This behavior could partially govern the kinetics of carbonation, performed in the presence of TBABr (3 wt%) as catalyst. Indeed, for a selected (*P*; *T*), TEFAD was more easily converted into TCFAD compared to IEFAD. The polyurethanes obtained by polyaddition of CFAD monomers with diamines (IPDA and EDA) exhibit molecular weights up to 13 500 g mol⁻¹ and glass transition temperatures around -15 °C. Interestingly, the side reaction between amine and ester functions leading to amide linkages was not observed when the secondary diamine IPDA was used as the comonomer.

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